SURFACE MODIFICATION AND ENERGY ABSORPTION PROPERTIES OF KEVLAR FABRIC

SYNOPSIS

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1. Introduction

The guardians of our country too, need guards to protect their body from enemy's bullets. Many companies and scientists are doing researches in order to make a light weight, more flexible and comfortable body armours. A continuous integration of new materials and technology is essential in respect of keen curiosity about improving the ballistic protection, leading to a development of an advance, smart, flexible and lightweight armor. In present era, many researchers are putting their best efforts to improve properties of existing ballistic materials to provide an improved ballistic protection to the soldiers, police officers and other security personnel.

Fabric armour, such as Kevlar, Twaron and Spectra, has been extensively used for flexible personnel ballistic protection due to its high strength, high tenacity and lightweight characteristics [1]. The usual method to increase protection against more lethal ballistic threats is to add more layers of fabric or ceramic inserts at the expense of increased weight of the armour and reduced mobility of the user. The effectiveness of fabric armour depends on several like the material properties of the yarns, the interaction between individual fabric layers, the fabric architecture, the projectile geometry far field boundary conditions; and the inter-yarn and fabric-projectile friction. Inter-yarn and fabric-projectile friction plays a significant role in the ballistic performance of the fabric and has been a subject of study of numerous researchers [2]. Lee et al. reported that yarns within woven fabric armor are less likely to slip over one another and over the projectile when the inter-yarn and fabric-projectile friction are increased. Hence, the projectile is required to engage and break more yarns instead of simply pushing the yarns apart in order to perforate the fabric. This results in increased energy absorption. The surface modification of Kevlar fabric by grafting is one of commonly used method to increase yarn friction hence the ballistic resistance of the fabric. It result to increase the ballistic limit of the fabric with decreasing levels of lubrication, leading them to conclude that modest changes to the inter-yarn friction could produce considerable changes in the ballistic performance of a fabric [3]. Hard plates are usually formed of Metal or ceramic plates or hot compressed polymeric materials and used with a soft vest for protection against high energy rifle rounds and used by combat soldiers, police tactical units, private citizens, and hostage rescue teams Bulletproof materials work by absorbing the kinetic energy of the fired shot and dissipating it so that the speed of the bullet reduces to nearly zero, which decreases the penetrating power and damage that is done. When

a bullet hits a Kevlar vest, it gets caught in the web of strong fibers, which absorbs and dissipates the energy, drastically reducing the impact of the bullet. This happens because the fibers are lined up so tightly that it takes a great deal of energy to separate them. Sometimes, the vest is strong enough to cause the bullets that hit it to become distorted or bent. Obviously, the more layers of Kevlar sheets, the greater the absorption power. Depending on the grade of Kevlar used and the number of layers, vests can more or less be more bulletproof. By the mid-to-late 1980s, an estimated 1/3 to 1/2 of police patrol officers wore able vests daily. By 2006, more than 2,000 documented police vest "saves" was recorded, validating the success and efficiency of lightweight able body amour as a standard piece of everyday police equipment.

1.2 Recent Development in Personal Protective Systems:

The primary objective of body amour research is to develop low cost, lightweight amour. The currently used body amours for military purpose are heavy in weight hence providing less mobility to the wearer. The demand for improving body amour is increasing day by day because if the penetration depth exceeds wearer can acquire serious blunt trauma. A material is needed which can offer the equivalent ballistic performance of existing body amour materials, but having low cost and flexibility.

A team of researchers from the University of Wollongong, have recently developed a new graphene composite material which is stronger than spider silk and Kevlar. Finding the right ratio of graphene to carbon nanotube is a key factor in the development of the bullet proof composites. The new graphene composite can easily be made using a wet-spinning method, producing fibers, which have potential applications in bulletproof armor, and reinforcement materials.

Carbon nanotubes have also been used extensively in the pursuit for Nano bullet proof materials. With a beehive shaped structure and cylindrical nature, these nanotubes have demonstrated incredible strength. These tubes are capped at each end and formed together with covalent bonds to produce nanofibers that are hundreds of times stronger than steel. Even the bonds themselves are stronger than those found in diamonds, the hardest substance known to man. The resulting carbon nanotubes are light, flexible, strong and thermally stable. In a bullet proof vest, millions of these nanotubes come together to form carbon nanofibers,

which are woven together to create and light weight material. The resulting carbon nanofibers are very good at absorbing energy making them ideal for bullet proof amour.

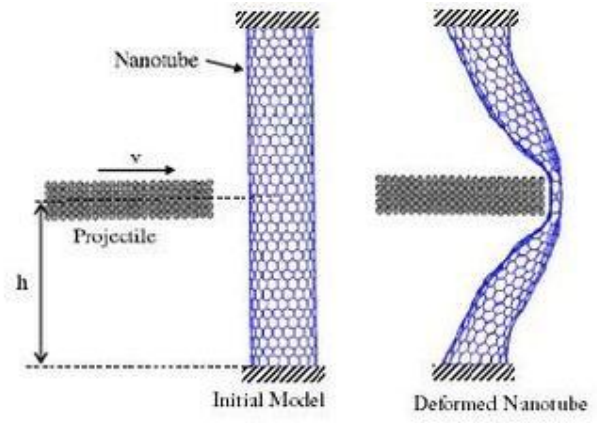


Figure 2.2: Impact of projectile on carbon nanotube

A team from the Centre for Advanced Materials Technology at the University of Sydney has already created a material, which can rebound the force of a bullet using these materials. Another example of this can be found in the Garrison Bespoke bulletproof suit. The suit uses a thin-patented carbon nanotube material, which sits between the linings of the suit. The suit protects the owner from stabbings, bullets and any other projectiles, which may cause harm.

1.3 Surface modification of Kevlar fabric to increase ballistic performance and yarn pull out behaviour.

Many surface modifications have been attempted on aramid fibres to improve their adhesion to polymer matrices.

Takayanagi et al. subjected a metallated aramid fibre to reaction with alkyl halides and bisphenol. A type epoxy resin 1'2. As a result of this reaction, the surface layer of aramid fibre was partly given functional groups. Evaluation of the interfacial adhesion between the modified fibre surface and an epoxy-amine resin by a pull-out test showed that surface modification of the aramid fibre by poly functional epoxy resin gave the highest adhesive strength. Andreopoulos performed the surface treatment of aramid fibre with various compounds and found that methacryloyl chloride was an effective coupling agent with possible grafting to the aramid fibre 3. Wertheimer and Schreiber modified an aramid fibre by plasma treatment to enhance the bond strength between the aramid and triazine 4. Eagles

et al. 5 performed two different surface treatments to improve the adhesion of aramid fibre to thermoplastic polymers, and showed that the sized aramid fibre had the greatest interfacial bond strength and frictional shear strength.

1.4 Functionalized monomers for surface grafting.

Functionalized polymers are of great importance because the specific properties of polymers are directly linked to functionality present in the polymers. Most common method of incorporation of a desired functionality in polymer involves the post polymerization or the post grafting reactions. These methods have a lot of advantages; however it suffers from the inherent property of the lowers reactivity of the polymers. Hence high temperature, long reaction time and strong reagents are required those often destroy original properties of the polymers. Therefore the synthesis of new monomers having desired functionality and their polymerization and grafting is of great importance to propose original materials of target applications.

2. **Literature Review**

Body armor or personal armor refers to protective clothing, designed to absorb and/or deflect slashing, bludgeoning and penetrating attacks by weapons. Coping and survival instincts led to early developments in body armors often taking the forms of protective clothing and primitive shielding devices. Body armors defined as any defensive coverings worn to protect the body from physical attacks which have evolved from readily available materials such as animal skins or natural fibers made from thatch, cotton, and silk often woven in textile forms to metals such as copper, steel, and iron used in plate and chainmail forms to the technologically complex armors used by today's armed services and law enforcement [4]. The body amours to be used by soldiers must be reliable so the weight, mobility and comfort become vital parameters for ensuring their use.

Regular non-plated personal amour is popularly known as soft body amour. For many years, our ancestors used various types of soft body amour such as animal skin, silk and nylon etc for protection from injury in combat. Nowadays, with advancement in technology it is composed of woven ballistic fabrics. Police, citizens and bodyguards use this type of armor. It provides protection to the wearer by resisting the low velocity bullet penetration. High performance aramid fabrics such as Kevlar and Ultra High Molecular Weight Polyethylene (UHMWPE)

fibers such as Dyneema are utilized for ballistic protection due to their high strength, low density and high-energy absorption. It consists of various layers of fabrics. When a bullet strikes the fabric, it gets caught in a web of yarns to which its kinetic energy is transferred [5]. Hence, two waves i.e. in-plane wave and transverse wave propagate from the point of impact. The kinetic energy dissipates from yarn deformations and inter-yarn friction when they slide against each other. Soft aramid fabric layers with considerable thickness allow a projectile to be stopped over a longer distance. Inter-yarn friction improves the ballistic performance till a critical value beyond which increase in friction may affect the dissipation of energy [6].

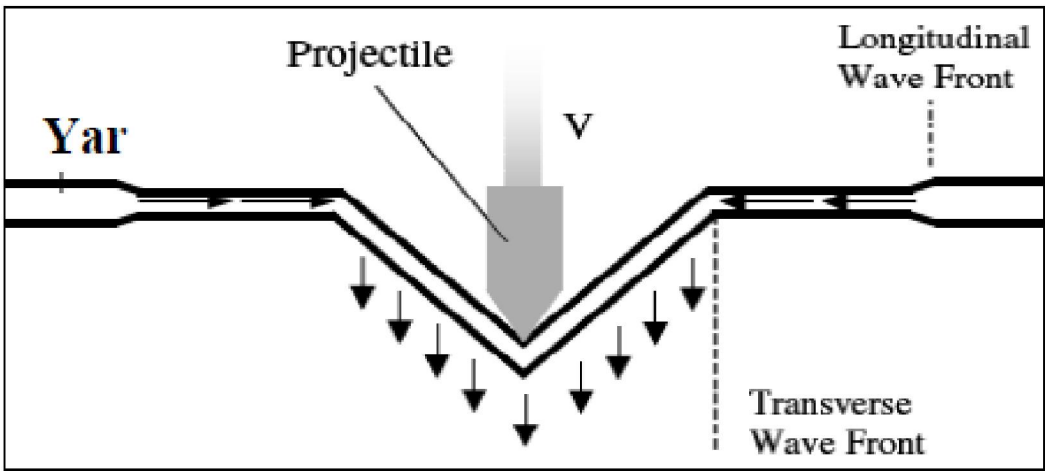


Figure 1.1: Wave transmission in body amour after striking of bullet[11]

Flexible woven fabrics are used for ballistic protection in body armor. These fabrics defeat the projectile through a combination of mechanisms, including yarn uncrimping, yarn stretching, yarn breakage, and yarn pull-out from the fabric [7]. The mechanisms that dominate a particular ballistic event depend on a number of factors, including the fabric material and architecture [8], as well as the projectile size, shape, and velocity [9]. However, the precise relationship between these mechanisms and the ballistic performance of fabrics is not fully understood.

Yarn pull-out from woven Kevlar fabrics is of particular interest. Kevlar fabric is the most widely used body armor material. It has shown that modifications to the frictional properties of the fabric can greatly alter, and often enhance, the ballistic performance of the fabric. Therefore, studying the yarn pull-out is an important first step toward understanding the role of yarn pull-out friction in fabrics, and eventually engineering frictional properties to enhance

their ballistic performance. The yarn pull-out experiments are performed at strain rates much lower than those experienced during a ballistic event. However, by conducting yarn pull-out experiments at low velocities comprehensive and systematic study of protection is possible.

The yarn pull-out test method is an experimental approach that evaluates these properties and is a bridge to fabric ballistic resistance investigations. In yarn pull-out test, a selected yarn in the middle of a fabric is simply pulled out of the weave, and the pull-out force along with yarn displacement is recorded for the purpose of mechanical and inter-yarn property evaluation. Many variations to the yarn pull-out apparatus have been used for experiments. The earlier pull-out test approach was developed by Sebastian et al. [10] and Motamedi et al. [11] by mounting fabric on a frame, connecting a selected yarn to a hook, and moving the frame. They studied yarn pull-out from plain woven cotton fabrics. Martinez et al. [12] studied the friction force required to completely pull out a single yarn from Kevlar fabrics by loading a static pressure over the full area of the fabric. Both groups found that pull-out force increased as fabric length increased. Bazhenov [13] performed yarn pull-out test on Aramid fabrics with different yarn counts and denier. The experiment utilized a fabric holding fixture at the bottom that was flat on left and right sides and curved up as U-shape in the middle (referred to as PI-shape by the author). The free end of the pulled yarn was centered under the U-shape section and was therefore unconstrained, while the fabric was clamped by the flat sides. The transverse edges were also unconstrained.

Poly-paraphenylene terephthalamide (branded Kevlar), was invented by Polish-American chemist Stephanie Kwolek while working for DuPont in 1971. Kevlar is a heat-resistant and strong aromatic polyamide. When Kevlar is spun, the resulting fiber has a tensile strength of about 3,620 MPa i.e. nearly fives time that of steel and relative density of 1.44 g/cm3. The polymer owes its high strength to many inter-chain bonds. These inter-molecular hydrogen bonds form between the carbonyl and N-H centers. Kevlar maintains its strength and resilience down to cryogenic temperatures (-196˚C); in fact, it is slightly stronger at low temperatures. At higher temperatures the tensile strength is immediately reduced by about 10-20%, and after some hours the strength progressively reduces further [14].

There are several grades of Kevlar available:

Table 2.1: Properties and applications among the grades of Kevlar

Kevlar grades	Properties	Applications

Kevlar 29	Lower modulus than glass fibers. It is ideal because it is non-flammable and offers protection from high temperatures.	In industrial applications such as cables, asbestos replacement, brake linings. It is mostly used fiber for protective clothing.
Kevlar 49	Higher modulus E Than glass fibers.	Mostly used in cable and rope products.
Kevlar 68	Modulus E – 10 to 15 % lower than Kevlar 49	Air industry applications, Reinforcement for optical cables.
Kevlar 100	Colored version of Kevlar	Colored fibers
Kevlar 119	20% higher strain comparing to Kevlar 49. Higher – elongation, flexible and more fatigue resistant.	Reinforcement for elastomers (V-bells).
Kevlar 129	15 to 20% higher strength comparing than Kevlar 29. 30 to 35% higher modulus than Kevlar 29.	Higher tenacity for ballistic applications.

Table 2.2: Differences in the properties among the main grades of Kevlar[14]

Kevlar Grades	Tensile Strength (GPa)	Tensile Modulus (GPa)	Elongation (%)	Density (g/cm3)
29	3.6	83	4.0	1.44
49	3.6-4.1	131	2.8	1.44
149	3.4	186	2	1.47

Kevlar is polyamide prepared by combining para-phenylenediamine and terepthaloyl chloride. To avoid degradation and to minimize the side reactions poly-condensation reaction is carried out at 10-20˚C.

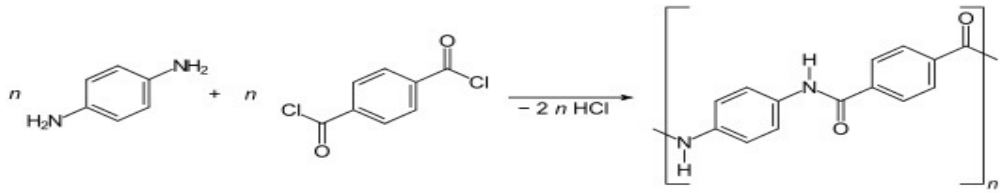


Figure 2.2 Preparation of Kevlar

Table 2.3: Reaction conditions for the preparation of Kevlar

Reaction	Solvent	Temperature (˚C)
Poly-condensation reaction	N-Methyl pyrrolidone (NMP)	10-20

Kevlar is often used in the field of cryogenics for its low thermal conductivity and high strength to other materials for suspension purposes. It is also used as a thermal standoff or structural support where low heat leaks are desired. Most famously, Kevlar is used in the making of personal armour such as combat helmets, ballistic face masks, and ballistic vests. The PASGT helmet and vest used by United States military forces use Kevlar as a key component in their construction. Civilian applications include: high heat resistance uniforms worn by firefighters, police officers, security and police tactical teams SWAT [14].Kevlar finds its great application in sports too as it is used for motorcycle safety clothing, especially in the areas featuring padding such as shoulders and elbows, in fencing it is used in the protective jackets, breeches and bib of the masks. Speed skaters also frequently wear an under-layer of Kevlar fabric to prevent potential wounds from skates in the event of a fall or collision. In 2013, with advancements in technology, Nike used Kevlar in shoes for the first time; this was done to decrease the elasticity of the tip of the shoe in contrast to nylon used conventionally as Kevlar expanded by about 1% against nylon which expanded by about 30%.What makes bullets so incredibly damaging is their very high speed. Of course, speed ranges from gun to gun, but they all move pretty fast! Rifles have bullets with a much higher speed- and hence more penetrating power- than bullets shot from revolvers. In 1976, Richard Davis, founder of second Chance Body Armor, designed the company's first all-Kevlar vest,

the Model Y [14]. Muntean, et al studied the Facile synthesis, characterization and magnetic properties of manganese ferrite/carbon composites[15]. Jacinth et.al. investigated the Synthesis and comparative studies of $MnFe_2O_4$ nanoparticles with different natural polymers by sol–gel method: structural, morphological, optical, magnetic, catalytic and biological activities [16].

3. Research Gap Identification

As we know Kevlar is widely used worldwide in protective systems. The interfarn friction play an importance role in arresting the projectile.. According to literature survey there is great scope in increasing performance of Kevlar fabric by surface modification of Kevlar fabrics. Furthermore the tailor made monomer can play a critical role in improving the performance of Kevlar fabric. As the Kevlar in para-armid system the incorporation of aryl group during the surface modification can further improve its performance.

4. Objectives

In fact there is enormous scope to improve the energy absorbing capacity of kevlar but the main objectives of this study are:

(i) To synthesize aryl acryloyl monomer for grafting on Kevlar fabric.

(ii) Characterization of the monomer by FTIR, ^{1}H NMR & ^{13} C NMR.

(iii) Surface grafting of synthesized monomer on Kevlar fabrics.

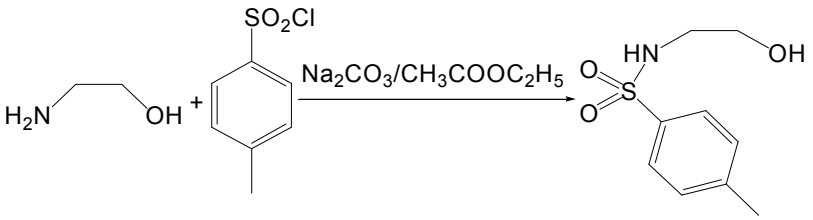
(iv) Yarn pull out test of surface modified Kevlar fabric and to compare its property with uncoated Kevlar fabric.

(v) Development of soft armor panel of modified Kevlar fabric.

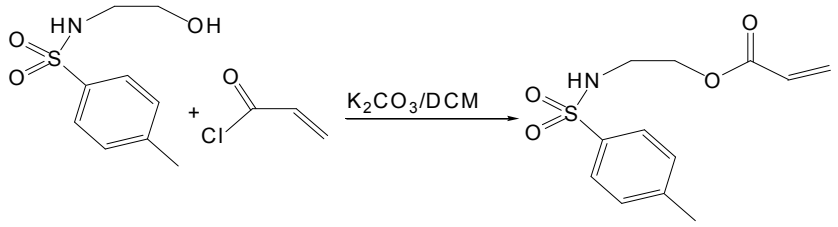
(vi) Ballistic Testing of newly developed Kevlar fabric panel.

5. Proposed Methodology:

(i) Synthesis of acrylic acid-2-(toluene sulphonyl amine)-ethyl ester (AATSAEE):



N-(2-Hydroxy-ethyl)-4-methyl-benzenesulfonamide



Acrylic acid 2-(toluene-4-sulfonylamino)-ethyl ester

(ii) Synthesis of monomer acrylic acid 2-(toluene-4-sulfonylamino)-ethyl ester (AATSAEE). Synthesis of monomer will be carried out in two steps as shown in figure 1 .

(iii)Synthesis of N-(2-hydroxy-ethyl)-4-methyl-benzene sulfonamide

(iv) Synthesis of N-(2-hydroxy-ethyl)-4-methyl-benzene sulfonamide involves chemospecific attach on NH_2 of ethanol amine with p-toluene sulfonyl chloride.

(v) Synthesis of acrylic acid 2-(toluene-4-sulfonylamino)-ethyl ester (AATSAEE)

The monomer will be obtained by the nucleophilic reaction of acryloyl chloride with 4a in the presence of triethylamine used as an acid scavenger.

vi. **Characterization of AATSAEE:**

The synthesized monomer will be characterized by FTIR, ^{1}HMR, ^{13}C NMR & LCMS.

vii. Surface Grafing of AATSAEE on Kevlar fabric:

Yarn pull out behaviour of surface modified kelvar fabric.

Ballistic testing of soft armor panel made of surface modified Kevlar fabric.

6. Thesis Outline:

Thesis shall comprise four chapters as:

Chapter 1 (Introduction): This chapter includes the introduction of bullet proof material, Kevlar fabric, tailor made monomers, yarn pull out test, ballistic testing and recent advances in bullet proof materials).

Chapter 2(Literature Review): This chapter includes the Literature Review of bullet proof material, Kevlar fabric, tailor made monomers, yarn pull out test, ballistic testing and recent advances in bullet proof materials.

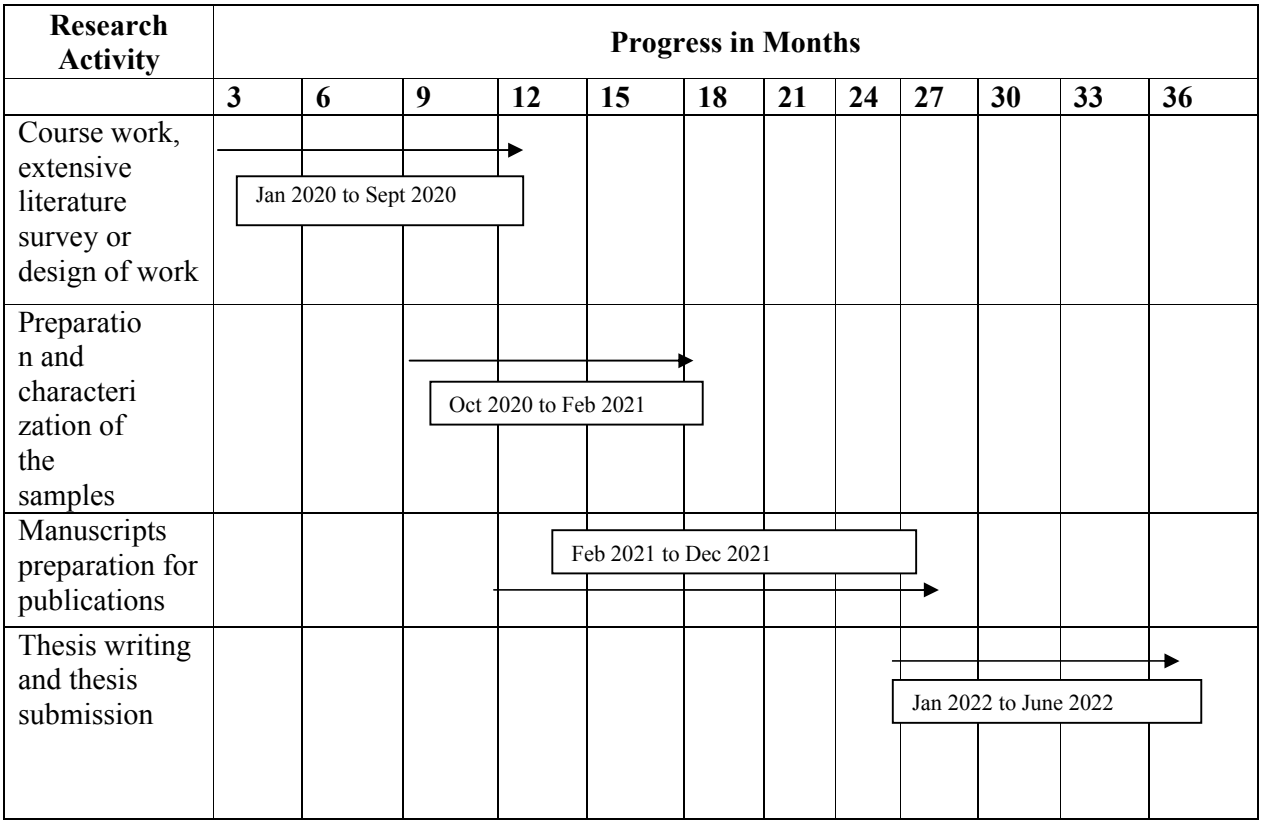
Chapter 3 (Materials and Methods): It includes the synthesis of tailor made monomer AATSAEE in multiple step process. The detailed characterization of monomer will be discussed in the chapter. This chapter will deal with surface modification of Kevlar fabric with AATSAEE. The modified Kevlar will be characterized by TGA and FTIR analysis. It will include the yarn pull out behaviour of Kevlar fabric, designing of soft armor panel and ballistic performance of designed soft armor panel.

Chapter 4(UV **Spectroscopy, FTIR, TGA, TEM):** Result and discussion.

Chapter 5 (Summary and Conclusion): This chapter will Comprises summary of entire study according to objectives along with conclusions. The scope of further research on the basis of recommendations shall also be included in this chapter.

Chapter 6: Reference

7. **Research Plan Schedule:**



References

[1] Kaur, H., Sharma, V., Jindal, S., Dhupar, A., Sharma, S. K., and Kumar, G. (2018, December). Structural and optical study of mixed Mg-Mn nanoferrite. In *AIP Conference Proceedings* (Vol. 2050, No. 1, p. 020010) 2018.

[2] Valenzuela, R. (2012).Novel applications of ferrites. *Physics Research International*, *2012*.

[3] Brown, J. (2005). Understanding how ferrites can prevent and eliminate RF interference to audio systems. *XP055206382, http://audiosystemsgroup. com/SAC0305Ferrites. pdf*.

[4] Saxena, N. K., Kumar, N., and Pourush, P. K. S. (2009). LiTiZn-Ferrite Radome for Satellite Communication. *Nature and Science*, *42*(44), 9.

[5] Laurent, H. J., and Carvalho, C. A. (1962). Ferrite antennas for am broadcast receivers. *IRE Transactions on Broadcast and Television Receivers*, (2), 50-59.

[6] Smit, J., and Wijn, H. P. J. (1959). Ferrites, Philips technical library. *Eindhoven, The Netherlands*, *278*.

[7] Kumar, G., Shah, J.,and Kotnala, R. K. (2015). Sarveena, Godawari Garg, Sagar E. Shirsath, Khalid M. Batoo, M. Singh. *Mater. Res. Bull*, *63*, 216.

[8] Wahba, A. M., and Mohamed, M. B. (2014). Structural, magnetic, and dielectric properties of nanocrystalline Cr-substituted $Co_{0.8}Ni_{0.2}Fe_2O_4$ ferrite. *Ceramics International*, *40*(4), 6127-6135.

[9] Ramesh, R., and Spaldin, N. A. (2007). Multiferroics: progress and prospects in thin films. *Nature materials*, *6*(1), 21.

[10] Deng, B., Li, Y., Tan, W., Wang, Z., Yu, Z., Xing, S., ... and Zhang, H. (2018). Degradation of bisphenol A by electro-enhanced heterogeneous activation of peroxydisulfate using Mn-Zn ferrite from spent alkaline Zn-Mn batteries. *Chemosphere*, *204*, 178-185.

[11] Carta, D., Casula, M. F., Falqui, A., Loche, D., Mountjoy, G., Sangregorio, C., and Corrias, A. (2009). A structural and magnetic investigation of the inversion degree in ferrite nanocrystals MFe_2O_4 (M= Mn, Co, Ni), *The Journal of Physical Chemistry C*, l113, 8606-8615.

[12] Desai, I., Nadagouda, M.N., Elovitz, M., Mills, M. and Boulanger, B., (2019). Synthesis and characterization of magnetic manganese ferrites. *Materials Science for Energy Technologies*, *2*(2), pp.150-160.

[13] Arshad, M., Asghar, M., Junaid, M., Warsi, M.F., Rasheed, M.N., Hashim, M., Al-Maghrabi, M.A. and Khan, M.A., 2019. Structural and magnetic properties variation of manganese ferrites via Co-Ni substitution. *Journal of Magnetism and Magnetic Materials*, *474*, pp.98-103.

[14] Kafshgari, L.A., Ghorbani, M. and Azizi, A., (2019). Synthesis and characterization of manganese ferrite nanostructure by co-precipitation, sol-gel, and hydrothermal methods. *Particulate Science and Technology*, *37*(7), pp.904-910.

[15] Muntean, E., Stoia, M. and Păcurariu, C., (2018). Facile synthesis, characterization and magnetic properties of manganese ferrite/carbon composites. *Thermochimica acta*, *667*, pp.122-131.

[16] Jacintha, A.M., Umapathy, V., Neeraja, P. and Rajkumar, S.R.J., (2017). Synthesis and comparative studies of $MnFe_2O_4$ nanoparticles with different natural polymers by sol–

gel method: structural, morphological, optical, magnetic, catalytic and biological activities. *Journal of Nanostructure in Chemistry*, *7*(4), pp.375-387.

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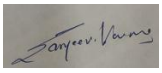

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